

Title:

"Desulphurization of ferrous materials using sodium silicate"

Cross-reference to related applications: **None**

5 Federally sponsored statement: **N/A**

Reference listing: **None**

Description

FIELD OF THE INVENTION

The present invention relates to (1) the use of a sodium compound as the primary desulphurizing reactant in a reactive desulphurizing agent, (2) the option of including other 5 desulphurizing reactants obtained from other reactive alkali oxides, alkaline oxides or other chemical compounds and metallic solids, (3) the method for producing the sodium-based reactive desulphurizing agent, (4) the process of applying the sodium-based reactive desulphurizing agent to a molten ferrous material and (5) the process for the deoxidation or reduction of the iron oxide in a molten ferrous material.

10 BACKGROUND OF THE INVENTION

Ample agreement exists on the growing need for low sulphur steels. In most types of steels, the presence of sulphur above 0.015% is undesirable. The increasing stringent requirement for better desulphurization of steel is attributed to the need for producing high strength low alloy steel and steels resistant to hydrogen induced cracking. In addition, even 15 minute contents of sulphur has pernicious effects on the manufacturing and finishing of steel products, such as brittle fractures in welding and fabrication, a tendency to separate along grain boundaries when stressed or deformed at temperatures near the melting point during the hot rolling phase in sheet steel processing, and even the influences on as-cast and the processing characteristics of the steel in terms of the workability of surface finish.

20 The desulphurizing of molten ferrous materials comprises thoroughly permeating the molten material with a reactive desulphurizing agent consisting of (1) metal oxides for replacing

the sulphur from the iron and for providing the flux required to float out the spent reactants and (2) the addition of solid metals to complete the deoxidization or reduction the iron. U.S. Pat. No. 4,014,685 teaches the four essential factors, for achieving good desulphurization in either a molten iron or steel, using a reactive desulphurizing agent. The factors are (1) high desulphurizing agent basicity, (2) high temperature on desulphurizing agent contact with the molten material, (3) low oxygen potential and (4) high desulphurizing agent fluidity.

Over the past several decades, a multitude of methods and processes have been set forth for the desulphurization of ferrous molten materials. Most of these methods are based on the reactions of a lime, fluorspar, aluminum oxide, alkali and alkaline metals or alloys, as well as the use of other reactants. An example of these methods is in U.S. Pat. No. 3,779,739, which teaches the art of desulphurization using calcium oxide and aluminum oxide or calcium oxide and calcium fluoride, wherein the calcium oxide increases the basicity of the desulphurizing agent and the aluminum oxide and calcium fluoride increase the fluidity of the desulphurizing agent.

Magnesium oxide has also been advanced in the art of desulphurizing ferrous materials, specifically metallic magnesium in U.S. Pat. No. 6,383,249.

Sodium, like magnesium, is a highly reactive metal, thus a high-performing desulphurizer that allows for a very high sulphur replacement in molten ferrous materials. However, because of its high reactive property, metallic sodium is highly unstable at ambient temperatures and violently reactive at the temperatures of a molten ferrous material and thus vaporizes explosively on contact with molten ferrous materials, hence metallic sodium, by itself, is ineffectual in removing sulphur. A preferred composition for the effective use of sodium as a desulphurizer is a chemical compound, such as in an oxidized state in combination with a flux-enhancing

compound. A far-reaching attractive feature in advancing the art of using sodium over magnesium as a desulphurizer is the availability of sodium compounds at a significantly lower cost.

The art of using sodium oxide, derived from sodium carbonate, as a reactant in a

5 desulphurizing agent is described in U.S. Pat. No. 4,014,685, U.S. Pat. No. 4,956,010, and U.S. Pat. No. 4,353,739. In none of these examples, where the art of using sodium oxide as a reactant in a reactive desulphurizing agent is put forth, is the art advanced wherein sodium silicate is used as the source of the sodium oxide desulphurizing reactant. Nor is a mention made on the preferred form for using a sodium silicate composition as the sole desulphurizer reactant in a

10 desulphurizing agent.

By itself, the melt point of SiO_2 is about 1580°C. However, once the SiO_2 is mixed or combined with other oxides such as Na_2O , the melt point of the resulting composition is much lower, around 700°C. The low melt point is an important and practical industrial property. On contact with the molten ferrous material, less thermal energy is required to dissolve the solid

15 sodium silicate reactive desulphurizing agent; thus, less caloric energy is necessary to maintain the ferrous material in its molten state as the sulphur replacement progresses. Hence, the use of sodium silicate as a desulphurizing agent is an efficient and effective method for removing sulphur from ferrous materials.

SUMMARY OF THE INVENTION

20 A method is disclosed for removing sulphur in molten ferrous materials using a sodium-based reactant in a reactive desulphurizing agent. The preferred reactant in the reactive desulphurizing agent is sodium silicate. A lime, dolomite, an alumina or mixtures thereof, may

optionally be added to enhance the replacement of the sulphur and control of the fluidity of the spent reactants in the molten ferrous materials.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a reactive desulphurizing agent is sodium silicate,

5 wherein the chemical composition of the sodium silicate comprises of y parts of SiO₂ to x parts of Na₂O and wherein, yet further, the ratio, y/x, is anywhere from 0.5 to 5. The SiO₂ and the Na₂O are fused at high temperatures. In the preferred embodiment of the invention the fusion takes place in a glass tank at temperatures from 900 to 1500°C. Other types fusion units, such as a rotary furnace, can also be used for the present invention provided the end results are consistent

10 with the intent and scope of the invention.

The sodium silicate reactive desulphurizing agent is brought into intimate contact with sulphur-laced molten ferrous materials. In the preferred embodiment of the invention, the molten ferrous material is drawn, in predetermined amounts, and laid in a layer to cover the surface of a desulphurizing vessel. The layer of molten ferrous material is then covered by a predetermined

15 amount of sodium silicate reactive desulphurizing agent. The process is repeated at least once until all the molten ferrous material available is desulphurized within the volume capacity of the vessel. As the desulphurization of the molten ferrous materials progresses, the spent reactants fluidize the surface and are removed from the desulphurizing vessel. To complete the reduction or deoxidation of the iron, a metallic solid is introduced into the molten ferrous material. In the

20 preferred embodiment of the invention the metallic solid is an aluminum rod.

In another embodiment of the invention, the reactants of the reactive desulphurizing agent comprise: sodium silicate, as prepared in the preferred embodiment, and oxides of calcium,

magnesium and aluminum. The preferred materials for said oxides are a lime compound such as limestone, dolomite and an alumina composite, respectively.

According to the invention, the preferred composition of the reactants in reactive desulphurizing agent, without the carbon dioxide comprises:

5 Na₂O from about 7 to about 50%
 SiO₂ from about 7 to about 50%
 CaO is ≤ 45%
 MgO is ≤ 8%
 Al₂O₃ is ≤ 25%

10 These and other advantages and features of the present invention will be more fully understood with the examples thereof.

EXAMPLE 1

A reactive desulphurization agent, based on sodium, was prepared from a composition of a sodium silicate and oxides of aluminum, magnesium and calcium. The parts ratio of the silicon oxide to the sodium oxide was 2.3:1, resulting in a sodium silicate composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. In addition to the sodium silicate composition, alumina, dolomite and lime were added in the amounts given in Table 1. The components were combined using a blade mixer in three approximately equal batches to obtain consistent mixtures. The weight percentages of the oxides in the unspent reactive desulphurizing agent are listed in Table 2. After mixing, the components were placed super-sacks and shipped to the site of the Basic Oxygen Furnace (BOF).

Table 1.

Desulphurizing Agent Component Weight	
Component	Kg
Sodium silicate	234.5
Alumina	284.1
Dolomite	218.8
Lime	535.4
Total 1272.8	

Table 2.

Desulphurizing Agent Composition (pbw)	
Reactive Oxides	Percent by Weight
CaO	53.33%
Na ₂ O	7.19%
MgO	5.70%
Flux Enhancers	Percent by Weight
Al ₂ O ₃	18.35%
SiO ₂	15.42%
Total 100.00%	

5 At the BOF site, initially, 70 metric tons of molten steel were drawn into a tap vessel and covered by 400 kg of the sodium-based reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered the sodium-based reactive desulphurizing agent. The controls parameters were maintained constant to provide oxygen at 356ppm. A solid metallic aluminum wire was injected

into the molten steel to deoxidize the iron oxide, with the oxygen reduced to 2.5ppm. During the desulphurization of the molten steel, neither the presence of toxic vapors nor the presence of sodium where detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent remained dissolved and fluid during the desulphurization process.

- 5 Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.012% to about 0.0088%.

EXAMPLE 2

In the second example, the sodium-based reactive desulphurizing agent based again was prepared from a sodium silicate and oxides of aluminum, magnesium and calcium. The parts

- 10 ratio of the silicon oxide to the sodium oxide was maintained as before, 2.3:1, resulting in a sodium silicate composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. However the amounts the sodium silicate composition, alumina, dolomite and lime added were slightly change, as given by weight amounts in Table 3. As before, the components where combined using a blade mixer in successive batches. The batch
15 weights for this example were not reported. The weight percentages of the oxide in the final sodium-based reactive desulphurizing agent composition are listed in Table 4. After mixing, the components were placed super-sacks and shipped to the BOF site.

Table 3.

Desulphurizing Agent Component Weight	
Component	Kg
Sodium silicate	225.8
Alumina	364.8
Dolomite	200.9
Lime	408.5
Total 1200.0	

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Table 4.

Desulphurizing Agent Composition (pbw)	
Reactive Oxide	Percent by Weight
CaO	45.50%
Na ₂ O	7.00%
MgO	7.00%
Flux Enhancers	Percent by Weight
Al ₂ O ₃	25.00%
SiO ₂	15.50%
Total 100.00%	

Essentially the desulphurization procedure at the BOF site, as outlined in Example 1, was repeated in this example, with the exception that the oxygen levels were lower both during the

desulphurization phase and the deoxidation phase. Initially, 70 metric tons of molten steel were drawn into a tap vessel and covered by 400 kg of the sodium reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered with a layer of the sodium reactive desulphurizing agent. The controls 5 parameters were maintained constant to provide oxygen at 226ppm. Metal aluminum wire was injected into the molten steel to deoxidize the iron oxide. In this example, the oxygen was reduced to 1.7ppm. During the process, neither the presence of toxic vapors nor the presence of sodium where detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent, as before, remained dissolved and fluid during the desulphurization 10 process. Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.0153% to about 0.0135%.

A further variation of the process consists of a number of sequential charges of lesser amounts of the molten steel charge and provide said molten charge with a layer of the reactive desulphurizing agent, wherein each layer of the reactive desulphurizing is in intimate contact 15 with the molten material.

It will be appreciated that the instant specifications and claims are set forth by way of illustrating and not limiting the present invention, and that various modifications and changes may be made without departing from the spirit, scope and intent of the present invention.